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DENSIFICATION OF ZIRCONIA WITH BORATES.(U)

JAN 80 A SIRCAR, R C BUCHANAN

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or 5 wt. % CaO borate ($\text{CaO} \cdot 2\text{B}_2\text{O}_3$; $\text{CaO} \cdot \text{B}_2\text{O}_3$) additions to these powders. Equivalent densities were obtained only at the 10 wt. % additive level for similar Y_2O_3 (12 wt%) ZrO_2 stabilized powders. Average grain sizes obtained for the more reactive B_2O_3 and $\text{CaO} \cdot 2\text{B}_2\text{O}_3$ additives at $1200^\circ\text{C}/4$ hours, were typically $< 1 \mu\text{m}$. Development of a monoclinic ZrO_2 phase was also observed in the sintered samples. This varied from ~ 7 -75 wt. %, and was approximately linearly dependent on the additive concentration. The effect was most marked for B_2O_3 additions to the CaO stabilized and least so with Y_2O_3 stabilized samples. This behavior was attributed to the progressive formation of a Ca borate phase with the B_2O_3 , in effect partially destabilizing the zirconia. This, however, results in increased thermal shock resistance.

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DENSIFICATION OF ZIRCONIA WITH BORATES,

BY

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A. Sircar and R. C. Buchanan

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Department of Ceramic Engineering
University of Illinois at Urbana-Champaign
Urbana, IL 61801

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ABSTRACT

Sintering studies carried out on submicron CaO (6.5 wt%) stabilized ZrO_2 powders, showed borate additions (1-10 wt.%) to be effective densification aids. Densities $> 99\%$ estimated theoretical were obtained at $1200^\circ\text{C}/4$ hours, with 2 wt.% B_2O_3 or 5 wt.% Ca borate ($\text{CaO}\cdot 2\text{B}_2\text{O}_3$; $\text{CaO}\cdot\text{B}_2\text{O}_3$) additions to these powders. Equivalent densities were obtained only at the 10 wt.% additive level for similar Y_2O_3 (12 wt%) ZrO_2 stabilized powders. Average grain sizes obtained for the more reactive B_2O_3 and $\text{CaO}\cdot 2\text{B}_2\text{O}_3$ additives at $1200^\circ\text{C}/4$ hours, were typically $< 1\text{ }\mu\text{m}$. Development of a monoclinic ZrO_2 phase was also observed in the sintered samples. This varied from $\sim 7\text{-}75\text{ wt. \%}$, and was approximately linearly dependent on the additive concentration. The effect was most marked for B_2O_3 additions to the CaO stabilized and least so with Y_2O_3 stabilized samples. This behavior was attributed to the progressive formation of a Ca borate phase with the B_2O_3 , in effect partially destabilizing the zirconia. This, however, results in increased thermal shock resistance.

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Densification of Zirconia with Borates

A. Sircar and R. C. Buchanan

I. Introduction

Stabilized zirconia solid solutions with CaO and Y_2O_3 are used extensively as refractory materials, and because of their high ionic conduction, as solid electrolytes for fuel cell and oxygen sensor applications.^{1,2} The sintering temperatures for commercial quality stabilized zirconia powders are in the range of 1700 to 1900°C. With very reactive, ultra fine powders,^{3,4} it is possible to get good densification at around 1450-1500°C.

The use of stabilized zirconia solid electrolytes for sensor applications generally requires precious metal, (Pt) electrodes. It would be economically advantageous to apply the precious metal electrode directly to the unfired ZrO_2 body and then by a single firing step obtain the densification of the electrolyte and intimately bonded conducting electrode. The limitation, in this case, is that the sintering temperature for the solid ZrO_2 should preferably be lower than the melting temperature of the electrode in order to prevent excessive volatilization losses. Significant advantages could therefore be obtained, in terms of energy saving, electrode costs and other problems associated with high temperature firing, if sintering of the stabilized ZrO_2 powders could be carried out at lower temperatures ($\sim 1200^\circ\text{C}$). One approach to bringing about this low temperature densification is by liquid phase sintering, using small amounts of a low melting ($< 1200^\circ\text{C}$) second phase as additive. The object of this investigation was

to explore the use and effectiveness of small amounts of selected borate compounds as densification aids for cubic stabilized zirconia powders. Calcium borate compounds were mostly used because of their high fluidity and stability at high temperatures.

II. Background

Low temperature densification of ceramic powders can be achieved in the presence of a liquid phase. The minimum requirements for good densification with liquid-phase sintering^{5,6,7} are:

- 1) sufficient liquid to permit wetting of the solid particles
- 2) appreciable solubility of solid in liquid
- 3) good wetting of the solid by the liquid

According to V. N. Eremenko et. al.,⁸ incomplete densification may occur if process variables are not properly controlled, for example:

- 1) the amount of liquid phase
- 2) the particle size of the solid phase
- 3) the compaction pressure

The liquid phase needed for the above purpose should have certain essential properties, namely:

- 1) The liquid phase if formed from the additive should have a low dihedral angle with the solid in order to achieve good wetting.⁹
- 2) The liquid phase if too highly viscous or too sparse could either hinder or lead to low densification rates.
- 3) The liquid should be uniformly distributed on a micro-scale throughout the body of the compact.

Most oxides are soluble in oxide liquids, but since diffusion rates in the liquid are significantly higher ($\sim 10^{-5} \text{ cm}^2/\text{sec}$), control

of grain growth normally depends on solubility in the liquid phase, as a rate controlling step.

For rapid densification to occur, the liquid should preferably be of low viscosity and non-glass forming. This allows for rearrangement of particles to take place with a minimum of liquid, but bond strengths in the composite solids could be low, depending on the amount and composition of the liquid phase. In contrast, a liquid which forms a glassy phase on cooling will give stronger bonding between particles, but more liquid is needed to cause particle rearrangement. The higher liquid viscosity also leads to lower diffusion and densification rates.

In practice, some compromise between the characteristic of these two types of liquids is often needed, to achieve good mechanical properties at reduced sintering temperatures.

In the present case, a boron oxide containing liquid was chosen as an additive because: 1) it is a glass former with a low melting point and viscosity; 2) the low diehedral angle formed by B_2O_3 containing liquids permits high penetration of the liquid phase between solid grains, as indicated by the harmful effects of very small smounts of B_2O_3 on magnesite refractories;^{10,11,12} 3) the volatilization loss of pure B_2O_3 at high temperatures suggests the possibility of utilizing it as a "fugitive" liquid for sintering purposes.

Cutler et. al.¹³ studied the effect of 1 wt% B_2O_3 on the sintering of monoclinic ZrO_2 and obtained a maximum density of 4.965 g/cm³ at 1700°C. However, Keler et al.¹⁴ concluded from their investigation of the effect of B_2O_3 on ZrO_2 solid solid solutions, that the efficiency of B_2O_3 as a sintering additive was negligible.

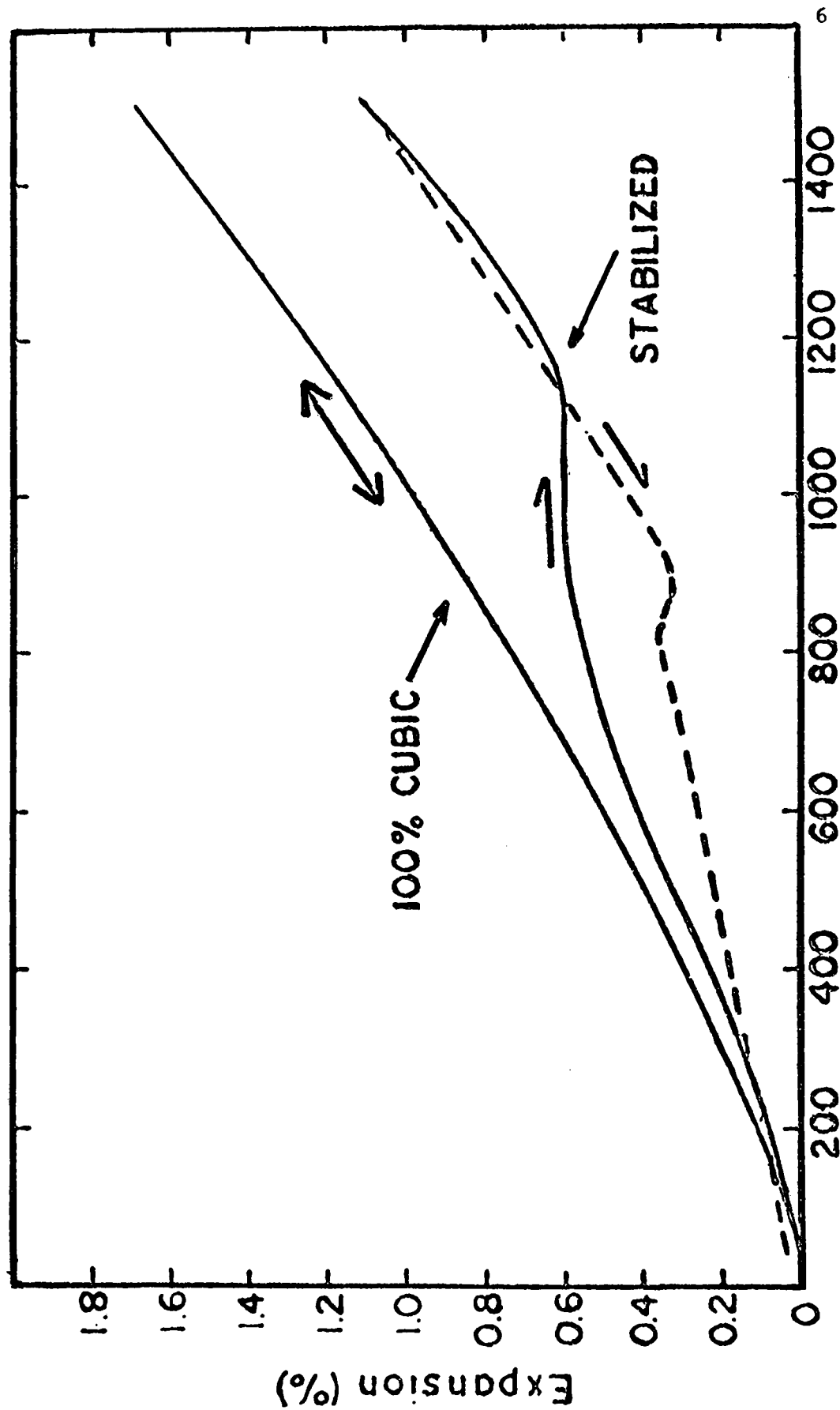
Boric oxide in combination with CaO and other RO type oxides forms borates which are very stable at high temperatures. Stuijts¹⁵ in fact found that $\text{CaO} \cdot \text{B}_2\text{O}_3$ was a very suitable sintering additive for making low porosity ferrite recording heads.

Several studies have been reported in the literature concerning the effects of additives on the sintering of ZrO_2 .^{13,16,17,18,19,20} Pure boric oxide as a lone additive is likely to combine with some of the stabilizing oxides (CaO or Y_2O_3) in the ZrO_2 solid solutions, leading to some degree of destabilization. To minimize this effect of pure B_2O_3 , two other borates were also used--calcium metaborate (CaOB_2O_3) with a congruent melting point of 1156°C and calcium tetraborate ($\text{CaO}_2\text{B}_2\text{O}_3$) which melts congruently at 986°C . Both calcium borates form low viscosity liquids above their melting points.

It should be pointed out, however, that partial destabilization of the cubic ZrO_2 can in many cases be beneficial. For example, incomplete stabilization of zirconia gives a body with better thermal shock resistance. This is because of the higher thermal expansion ($11\text{--}12 \times 10^{-6}$) and low coefficient of thermal conductivity ($1.72 \text{ K.Cal/m.h.deg.}$) of cubic zirconia. Partial stabilization reduces the modulus of elasticity and the coefficient of thermal expansion, and creates microcracked structures, which boost the resistance to thermal impact.

According to Curtis,²¹ the partially stabilized zirconia contains 10 to 20% of the low expansion ($7\text{--}8 \times 10^{-6}$) monoclinic form. Figure 1, shows the difference in expansion between completely and partially stabilized ZrO_2 .²²

Recently, Garvie and Nicholson²³ and Nicholson et.al.²⁴ attempted to correlate the previous work on the relationship between thermal



Temp. (°C.)

FIGURE 1. Thermal Expansion of Completely and Partially Stabilized ZrO_2 (after Whittmore and Ault).

expansion characteristic and thermal shock behaviour. These authors concluded that in partially stabilized zirconia a subgrain structure of pure (monoclinic) ZrO_2 is created in a cubic stabilized zirconia matrix. The monoclinic-tetragonal transformation induces in the pure ZrO_2 component a large volume of microcracks which enhances the thermal shock resistance. According to Karaulov et al.,²⁵ this enhanced thermal shock resistance was obtained in partially stabilized zirconia with an optimum of 30 wt% monoclinic ZrO_2 phase.

In fusion cast alumina-zirconia-silica (AZS) refractories, containing 34 to 41 wt% monoclinic ZrO_2 , a glassy phase is essential to cushion the thermal stresses arising from the monoclinic/tetragonal inversion at around 1150°C.

III. Experimental Procedure

1. Sample Preparation

The powders used in this study were calcia and yttria-stabilized zirconia containing, respectively, 6.5 wt% CaO and 12 wt% Y₂O₃ [Zircar Products Inc., Florida, N.Y.]. The as-received powders were reported to be highly reactive, of average particle size less than 0.1 μ m (crystallite size .02-.03 μ m) and to sinter to near theoretical densities in the temperature range 1450-1500°C). A few studies were also made using a much coarser particle size (~ 1-2 μ m ave.) cubic stabilized zirconia powder, "Zircoa B" [Zirconia Corp. of America].

The additives used as sintering aids were reagent grade boric anhydride, calcium metaborate and calcium tetraborate (made up by melting appropriate amounts of CaCO₃ and B₂O₃, followed by crushing and milling in CH₃OH). These were added in amounts of 2, 5 and 10 wt%. (Equivalent volume % are shown in Table I). Batches of 15 g were prepared by weighing the appropriate amounts of ZrO₂ and additive. The powders were milled in 250 cm³ polyethylene bottles using ZrO₂ grinding balls and methyl alcohol as dispersant. After milling for 4 to 5 hours, the powders were vacuum dried. Initially, no binders were used but it was later determined that for these ultrafine powders it was necessary to have a lubricant solution to achieve uniformly pressed pellets. Accordingly, a 1% solution of carbowax in methyl alcohol was added as binder solution. The amount was not optimized, but good pressed densities were obtained at this concentration.

TABLE I

Wt. and equivalent Vol. percent additive to CaO and Y_2O_3 Stabilized ZrO_2 Samples

Additive	wt%	Equivalent Vol. %	
		CaO_2 (6.5w/o) ZrO_2 ($\rho=5.5 \text{ gm/cm}^3$)	Y_2O_3 (12w/o) ZrO_2 ($\rho=6.05 \text{ gm/cm}^3$)
1. $\text{CaO} \cdot \text{B}_2\text{O}_3$ ($\rho=2.65 \text{ gm/cm}^3$)	2	4.06	4.45
	5	9.84	10.72
	10	18.74	20.24
2. $\text{CaO} \cdot 2\text{B}_2\text{O}_3$ ($\rho=2.73 \text{ gm/cm}^3$)	2	3.95	4.33
	5	9.59	10.45
	10	18.29	19.76
3. B_2O_3 ($\rho=2.46 \text{ gm/cm}^3$)	1	2.21	2.42
	2	4.36	4.78
	5	10.53	11.46
	10	19.90	21.46

Pellets of 1.25 cm diameter and 0.2 cm thickness were made by pressing in a hydraulic press, using uni-directional forming pressures of 22-40 Kpsi. Theoretically, the higher compaction pressure should increase densification. However, in practice, during the processing of the ultrafine powders, the higher compaction pressure produced more closed pores. This would be expected to reduce the capillary forces which aid liquid phase sintering and could also hinder particle rearrangement. Also higher compaction pressures were found to cause delaminations and sticking of pellets to the die body. Compaction pressures at the lower end of the range is, therefore, preferable.

The compacted pellets were placed on platinum foil and sintered in a SiC muffle furnace (with controlled heating and cooling rates) at temperatures of 1100°C, 1200°C and 1350°C (1450°C for CB_2 addition) for a soak.

2. Density Determination

The bulk density of the specimens were determined by using a mercury hydrometer (which gives an accurate measurement of bulk volume). It consisted of a solid cone made from Tantalum (density: 16.654 gm/cc), attached to a ~ 10 cm Tantalum rod with a hook at one end in order that it can be suspended from the balance hook of an accurate electric balance. The lower periphery of the cone had prongs to prevent displacement of the test specimens from the underside of the cone. In use, a glass beaker containing 400 cm³ of clean mercury was placed on a balance bridge over the balance pan. The Tantalum hydrometer, which was sprayed with a coat of acrylic varnish to prevent reaction with Hg, was immersed in the liquid Hg

and stirred well so that no air was trapped inside. The hydrometer was then suspended from the balance hook and its weight, W_1 noted. The test specimen was carefully slipped under the Tantalum specimen holder with a pair of tweezers without lifting the holder completely above the Hg surface (this was to prevent air being trapped between the test piece and the holder). The new weight of the hydrometer W_2 was determined, which is now lighter than W_1 , because of the displacement of mercury by the test piece. Thus, if $(W_1 - W_2)$ is the wt. of mercury displaced by the test piece, W_0 is the weight of test piece in air, and ρ is the density of mercury at the temperature involved (gm/cm^3), then the bulk density (BD) of the specimen can be obtained from the relationship:

$$\text{BD} = \frac{W_0 \times \rho}{W_0 + (W_1 - W_2)} \quad (1)$$

The apparatus could be balanced to ± 0.01 gm, corresponding to an error $\pm .001$ cc in volume, because of the high density of mercury (13.6 g/cm^3).

Calculation of theoretical densities of samples were obtained from volume % additives and the published theoretical densities of CSZ (5.5 g/cm^3), YSZ (6.05 g/cm^3), calcium metaborate (2.65 g/cc), calcium tetraborate (2.73 g/cm^3 -mercury displacement) and boric oxide glass (2.46 g/cm^3). The formula used was:

$$\frac{1}{\rho_{\text{th}}} = \frac{V_1}{\rho_1} + \frac{V_2}{\rho_2} \quad (2)$$

where V_1 and V_2 are the volume fractions of the respective phases with densities ρ_1 and ρ_2 . The relative density calculation (% Th.D) were made from the ratios of bulk and theoretical densities.

3. X-Ray Diffraction

Samples of the fired specimen were crushed and ground to very fine powders in an alumina mortar, and spread on a microscope slide using methyl alcohol. These samples were placed on a Norelco X-Ray diffractometer and irradiated by $\text{CuK}\alpha$ radiation using a Ni filter. The samples were scanned in the range of $2\theta = 26^\circ$ to 65° at a rate of $2^\circ 2\theta/\text{min}$. The monoclinic and cubic ZrO_2 peaks were identified by comparison with standard values obtained from the A.S.T.M. index for the pure cubic and monoclinic ZrO_2 phases. The total weight percent of monoclinic ZrO_2 was then estimated²⁵ by measuring the areas under the major diffraction peaks for cubic ($2\theta \approx 30.5$) and monoclinic ($2\theta = 28.65$) ZrO_2 .

4. Microstructural Examination

Fracture surfaces of the samples were studied in a JOEL-JSM U35 scanning electron microscope. The surfaces were coated with a thin film of Au ($\sim 200\text{-}500\text{\AA}$) by sputtering technique. Polished sections were not successfully prepared due to the difficulty with pull-outs during grinding and polishing.

Results

Sintering

Table II shows the bulk and % theoretical densities obtained for CaO stabilized ZrO_2 (CSZ) samples, containing 0 to 10 wt. % $\text{CaO} \cdot \text{B}_2\text{O}_3$ (CB), $\text{CaO} \cdot 2\text{B}_2\text{O}_3$ (CB_2) and B_2O_3 as additives. The samples were fired at 1100, 1200 and 1350° C (1450° C for CB_2) for 4 hours, followed by slow cooling to room temperature. The density data are shown plotted in Figures 2, 3, and 4 as a function of composition and temperature for the CB, CB_2 and B_2O_3 additives, respectively.

Sintering and density data for the Zircoa B sample with CB and CB_2 additions are shown in Table III.

Figure 2 shows that with no additives, the fired densities of samples sintered at 1100, 1200 and 1350° C were 59, 85 and 95% Th.D., respectively. For 2% CB addition, there is an increase in densification at 1100° C, very slight decrease at 1200° C and a significant decrease at 1350° C. This decrease could reflect the fact that insufficient liquid was present to aid densification by particle rearrangement or to accommodate the expansion of the monoclinic ZrO_2 phase which could be formed. At 1350° C, the viscosity of the liquid phase would be expected to be lower than at 1200° (m.p. of CB = 1154° C) resulting in greater relaxation of the pressed pellets, which is reflected in the large relative decrease in density. With 2 wt. % CB addition at 1100° C, it is assumed that no liquid is present and sintering is therefore, by solid state mechanism.

For 5 wt. % CB addition, the densification at 1100° C remained unchanged but some increase in density (66.7 to 71% Th.D.) was

TABLE II
Fired Densities for CaO-stabilized ZrO₂ (CSZ) Compositions

Compositions	Fired Densities 4 HOUR SOAK					
	1100°C		1200°C		1350°C	
	B.D.	% Th.D.	B.D.	% Th.D.	B.D.	% Th.D.
Pure CSZ (40 Kpsi) (22,000 Psi)	3.265 3.09	59.36 56.18	4.70 4.60	85.45 83.64	5.30 5.19	96.4 94.3 (1450°)
CSZ + 2 wt% CB (22,000 Psi) + 2 wt% CB ₂ + 2% B ₂ O ₃ (+ 1% B ₂ O ₃)	3.58 3.655 3.81 3.50	66.48 67.80 70.99 64.41	4.56 4.97 5.58 5.140	84.68 92.20 100.00 94.60	4.89 5.23 -- --	90.85 97.02 (1450°) -- --
CSZ + 5 wt% CB (22,000 Psi) + 5% CB ₂ + 5% B ₂ O ₃	3.47 3.90 3.70	66.48 74.50 71.43	5.16 5.24 5.19	98.85 100.00 100.00	5.28 5.31 --	100.00 100.00 (1450°) --
CSZ + 10% CB (22,000 Psi) + 10% CB ₂ + 10% B ₂ O ₃	3.535 4.216 3.40	71.2 84.44 69.46	4.93 5.115 4.85	99.4 100.00 99.18	4.93 4.89 --	99.40 97.90 (1450°) --

BD - Bulk Density; Th.D. - Theoretical Density; % Th.D. = $\frac{BD}{Th.D}$

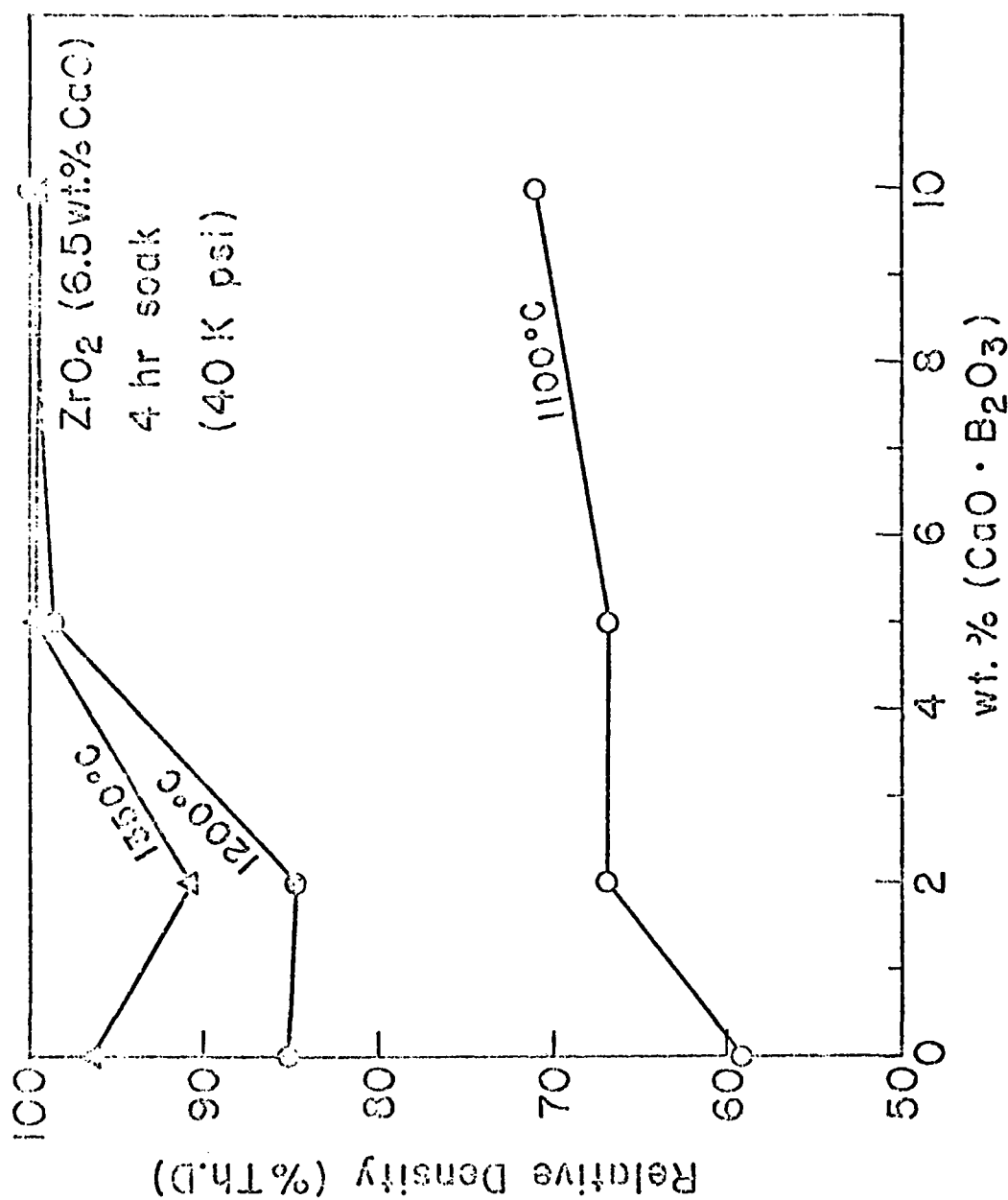


FIGURE 2. Effect of CaO·B₂O₃ addition on the densification of CaO (6.5 wt.%) -stabilized ZrO₂ (CSZ) samples.

observed when the CB concentration was increased to 10 wt %. This probably results from greater solid state densification of the CB phase along the ZrO_2 grain boundaries. At 1200°C , a significant increase in densification to approximately 99 % Th.D. was observed. Similar densification was noted for the 1350°C curve. This would indicate that the 5 wt % CB addition provided sufficient liquid to bring about densification by rearrangement and other liquid phase mechanisms. This is evident from the 10 wt % CB additions where essentially complete densification was achieved at 1200° and 1350°C .

For the CB_2 curve shown in Figure 3, the compaction pressure was 22,000 psi and also liquid phase was present above 980°C (the m.p. of CB_2), hence there would be less tendency for sample expansion with insufficient liquid. In consequence, higher densities were achieved for the 1100°C sintering, compared to the CB samples. The 1200 and 1450°C curves show increased densification with 2 wt% CB_2 and complete densification for 5 wt % CB_2 addition. At 10 wt % CB_2 addition there was some decrease in densification because of excess liquid phase, and some puddling was also observed.

Figure 4 shows that the addition of B_2O_3 to the CaO stabilized zirconia, increased the densities of sintered pellets, reaching a maximum for 2 wt % B_2O_3 at 1200°C . This may be attributed to the fact that the B_2O_3 combines with the CaO from the ZrO_2 to form low melting calcium borates, which are liquid above 1100°C . Even with one wt % B_2O_3 addition to CSZ, sufficient liquid was formed at 1100°C and 1200°C to give significant densification.

It is evident from the above observations that the amount of borate additive needed to bring about equivalent densification of CaO stabilized zirconia, increases in the order of $\text{B}_2\text{O}_3 > \text{CB}_2 > \text{CB}$.

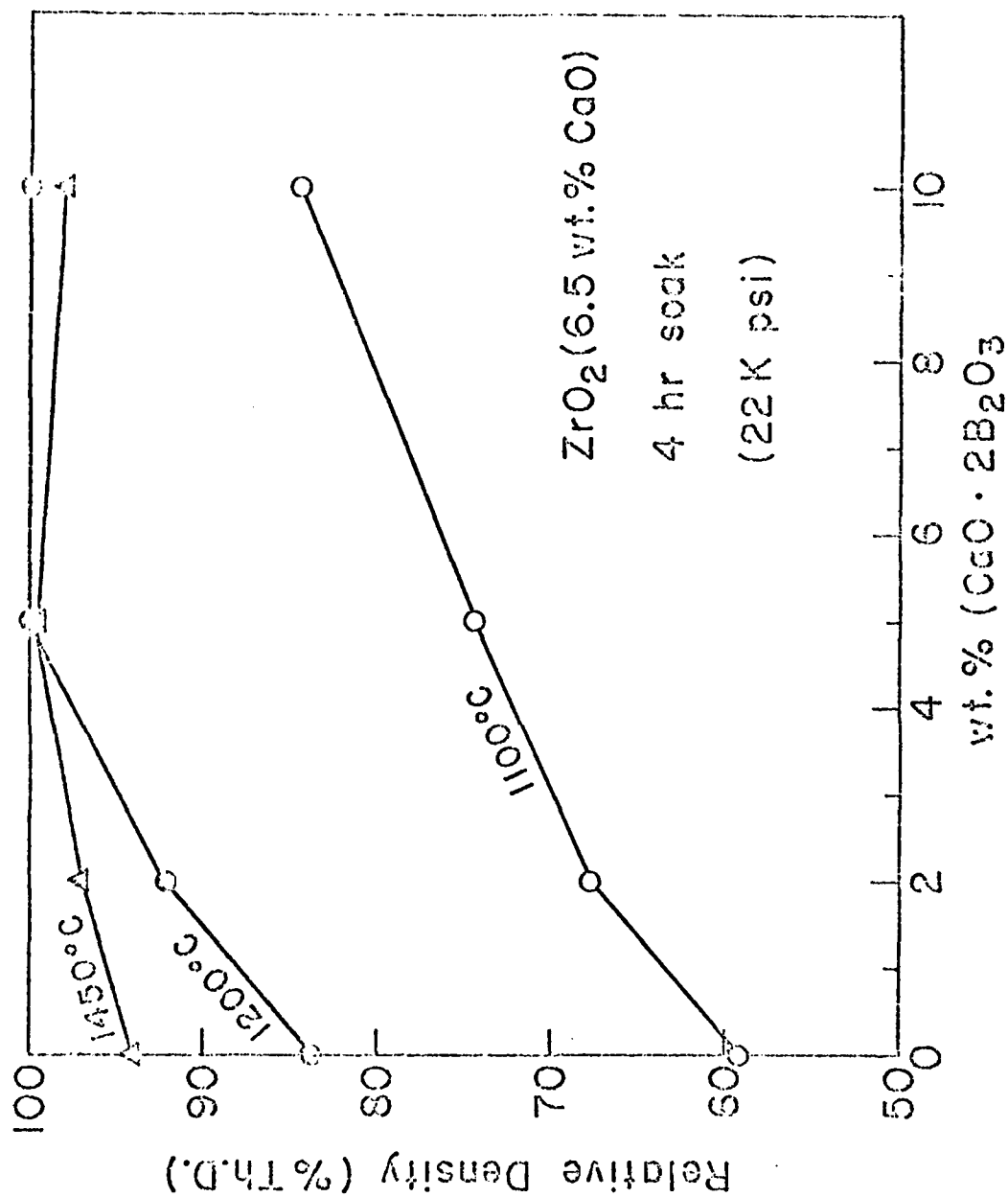


FIGURE 3. Effect of $\text{CaO} \cdot 2\text{B}_2\text{O}_3$ addition on the densification of CaO (6.5 wt.%) -stabilized ZrO_2 (CSZ) samples.

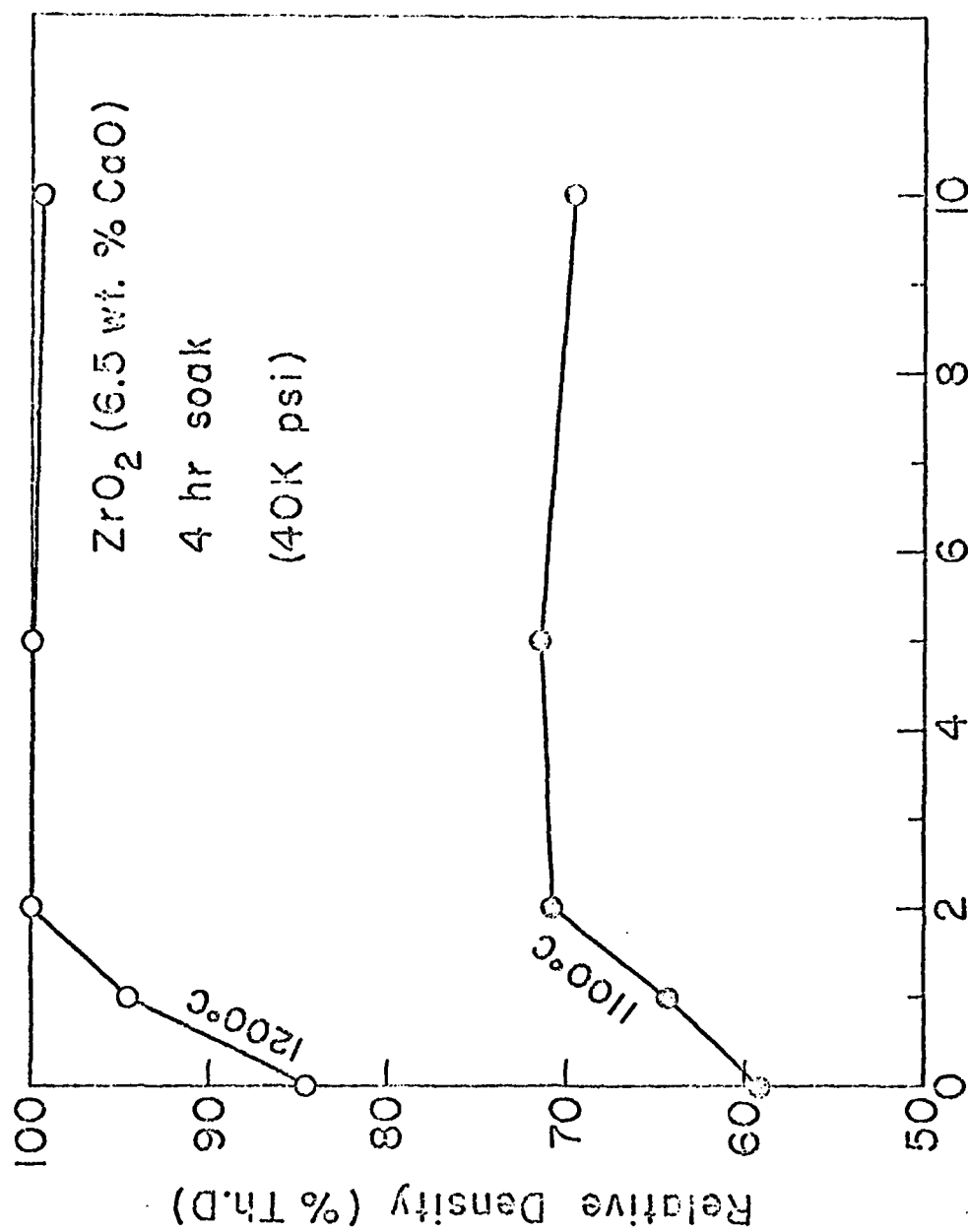


FIGURE 4. Effect of B₂O₃ addition on the densification of CaO (6.5 wt.%) -stabilized ZrO₂ (CSZ) samples.

This may be attributed to the fact that the liquid phase formed from the B_2O_3 is very reactive (lower viscosity, better wetting, higher solubility) and that this reactivity decreases with increasing CaO content in the liquid. Thus for 2 wt % CB_2 (3.95 volume %) the densification observed at $1200^\circ C$ was greater than for 2 wt % CB addition, although the volume % liquid formed (4.06%) is slightly larger in the latter case. For 2 wt % B_2O_3 addition (4.4 volume %), complete densification was achieved at $1200^\circ C$. Thus it is likely that higher amounts of liquid are present for the B_2O_3 additions, but it should be noted also that with these borate additives, CaO would likely be extracted from the cubic ZrO_2 lattice to form higher calcium borate compounds. The expected order of calcium removal in this case would be $B_2O_3 > CB_2 > CB$ and this process may also contribute to the observed densification behavior.

From Table III, it is observed that significantly lower densification was observed for Zircoa B compared with CSZ samples with equivalent sintering conditions and like additions of CB and CB_2 addition. This may be attributed to the lower reactivity of the Zircoa B powders (larger average particle sizes) as indicated by the fact that reasonable density of 93% Th.D. was achieved only above $1350^\circ C$ for 5 wt % CB_2 . Cracking of the samples at higher additive concentration may result from increased strain induced in the larger particle size ZrO_2 grains as conversion to the monoclinic phase takes place.

Table IV shows the bulk and % theoretical densities obtained for yttria stabilized ZrO_2 (YSZ) samples containing 0-10% $CaO \cdot B_2O_3$, $CaO \cdot 2B_2O_3$, and B_2O_3 . The samples were fired at 1100, 1200 and

TABLE III

Fired Densities for CaO (4.8 w/o) stabilized ZrO₂ (Zircoa B)* samples

Compositions		Sintering Temperatures/Densities (4 HRS. SOAK)					
		1200°C		1350°C		1450°C	
	Th.D.	B.D.	%Th.D.	B.D.	%Th.D.	B.D.	Th.D.
Zircoa B	5.5	3.98	72.33	4.447 4.40	80.9	4.47	81.3
2 wt % CB	5.385	--	--	4.276	79.4	4.31	80.11
2 wt % CB ₂	5.39	4.216	78.22	4.52	83.86	--	--
5 wt % CB	5.22	--	--	4.29	82.2	4.395	86.1
5 wt % CB ₂	5.23	3.962	75.72	4.84	92.56	cracked	
10 wt % CB		--	--	4.67	94.15	4.67	94.15
10 wt % CB ₂	4.99	4.09	81.96	cracked		cracked	

BD - Bulk Density; Th.D. - Theoretical Density; % Th.D. = $\frac{\text{B.D.}}{\text{Th.D.}}$

*Composition (wt.%): 93.5 ZrO₂; 4.8 CaO; 0.62 SiO₂; 0.25 MgO; 0.4 (R₂O₃)

TABLE IV
Fired Densities for Y₂O₃-stabilized ZrO₂ (YSZ) Compositions

Compositions	Fired Densities 4 HOUR SOAK							
	1100°C		1200°C		1350°C		Th.D.	
	B.D.	%Th.D.	B.D.	%Th.D.	B.D.	Th.D.		
Pure YSZ (40 Kpsi) (22 Kpsi)	3.91 3.66	64.63 60.5	5.50 5.40	90.91 89.26	5.85 5.75	96.69 95.04 (1450°C)		
YSZ + 2 wt % CB	3.942	66.83	4.71	79.84	4.86	82.39		
22 Kpsi + 2 wt % CB ₂	3.70	62.65	4.57	77.38	5.70	96.51 (1450°C)		
+ 2 wt % B ₂ O ₃	3.17	53.93	4.31	73.32	--	--		
+ 1 wt % B ₂ O ₃	3.27	54.84	4.58	76.81	--	--		
YSZ + 5 wt % CB	4.57	80.39	5.47	96.17	5.29	93.05		
(22 Kpsi) + 5 wt % CB ₂	4.47	78.38	5.29	92.76	5.62	98.54 (1450°C)		
+ 5 wt % B ₂ O ₃	3.21	56.92	4.27	75.72	--	--		
YSZ + 10 wt % CB	4.78	89.18	5.34	99.12	5.26	98.10		
(22 Kpsi) + 10 wt % CB ₂	4.82	89.27	5.396	100.00	5.30	98.26 (1450°C)		
+ 10 wt % B ₂ O ₃	3.186	60.37	5.22	98.90	--	--		

B.D. - Bulk Density; Th.D. - Theoretical Density; % Th.D. - $\frac{\text{B.D.}}{\text{Th.D.}}$

1350°C (1450°C for CB_2) for 4 hours followed by slow cooling to room temperature.

As seen from Figure 5, the fired densities of the YSZ samples without any additives were 64.6, 90.9 and 96.7 % T.D. at 1100, 1200 and 1350°C. At 1100°C, the densities of the fired samples increased with increasing amount of CB additive (this again is assumed to be by solid state processes in the absence of a liquid phase). However, with 2 wt % CB addition there was a decrease of fired densities at 1200 and 1350°C. This lowering of density may again be due to insufficient amount of liquid, causing an expansion in the compressed pellets. With further CB addition, the densities of the YSZ samples increased reaching a maximum for 10 wt. % CB. However, the lower densities observed at 1350°C for 5 and 10 wt % CB addition, compared to those obtained for similar addition at 1200°C may be due to pressing problems.

In Figure 6, the % theoretical densities of YSZ samples, fired at 1100, 1200 and 1450°C for 4 hours, are plotted as a function of the wt % calcium tetraborate (CB_2). There is a general increase in fired density with increasing amount of CB_2 for sintering temperatures of 1100, 1200 and 1450°C, except for the marked decrease with 2 wt % additive at 1200°C. The reason for this decrease is probably associated with decrease in viscosity with temperature of an essentially non-reactive liquid phase, leading to expansion of the compact.

Figure 7 shows the % T.D. obtained for YSZ samples fired at 1100 and 1200°C, as a function of the wt % B_2O_3 added. Both at 1100 and 1200°C, there was initially a lowering of fired densities

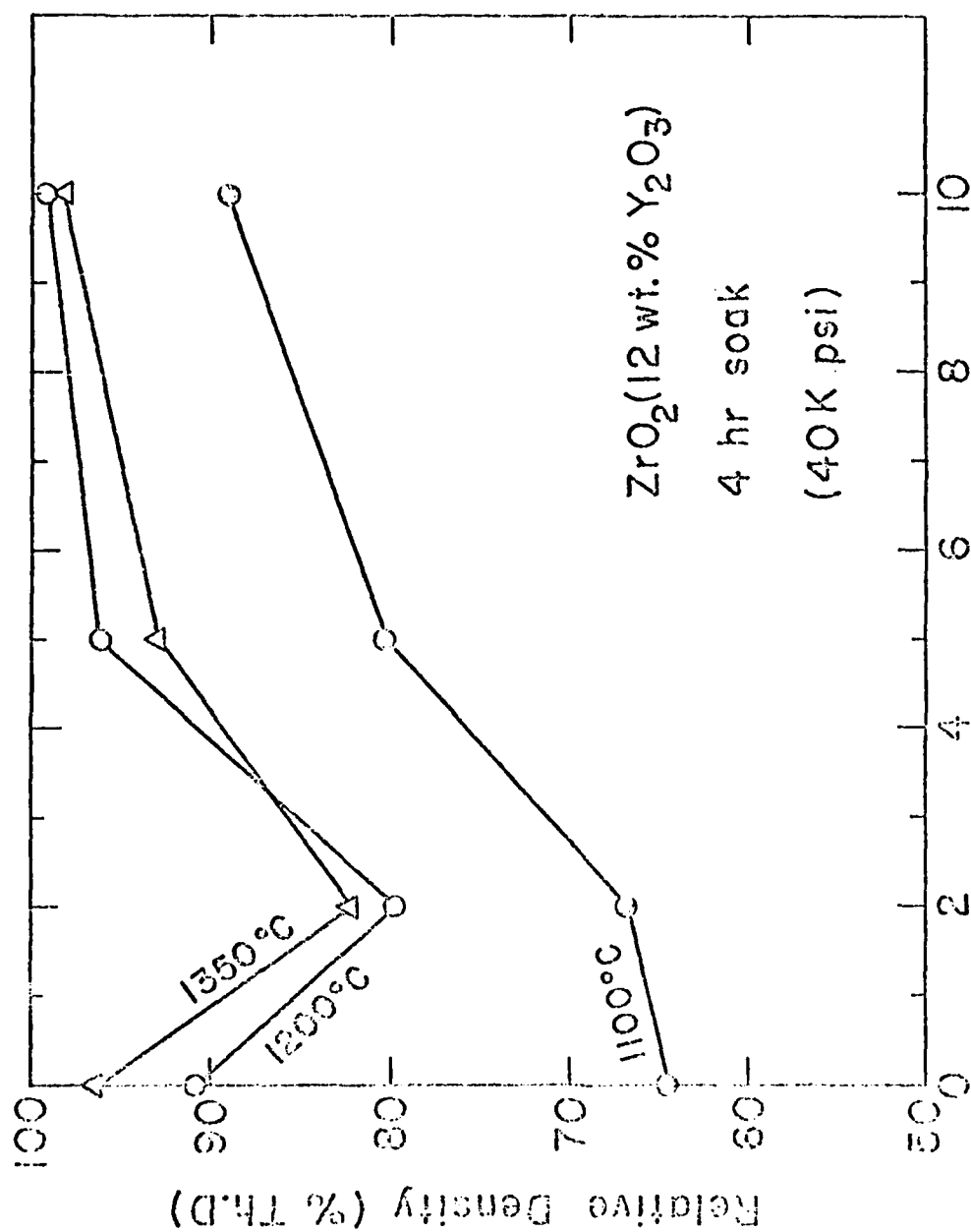


FIGURE 5. Effect of $\text{CaO} \cdot \text{B}_2\text{O}_3$ addition on the densification of Y_2O_3 (12 wt.%) -stabilized ZrO_2 (YSZ) samples.

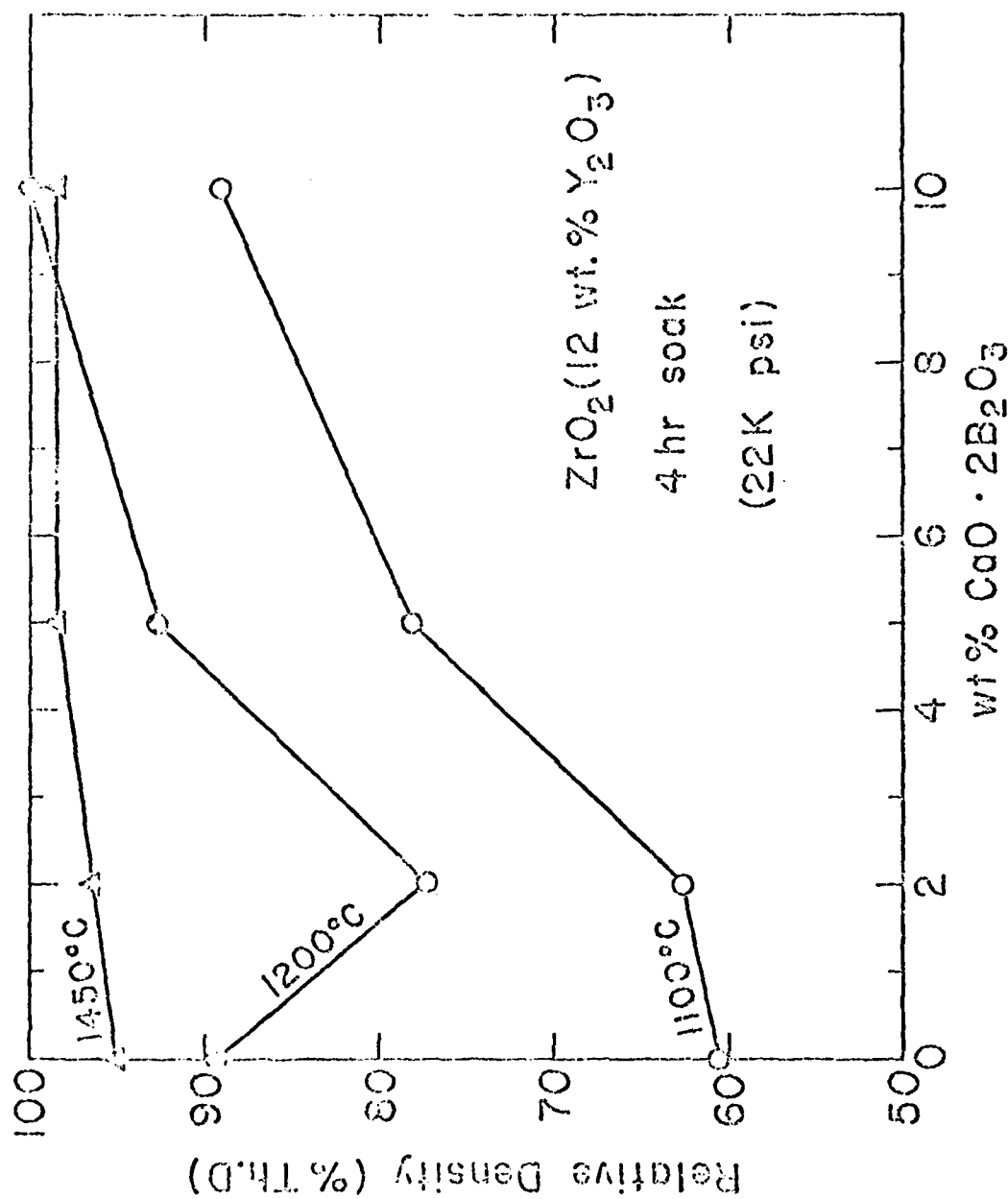


FIGURE 6. Effect of $\text{CaO} \cdot 2\text{B}_2\text{O}_3$ addition on the densification of Y_2O_3 (12 wt.%) -stabilized ZrO_2 (YSZ) samples.

with the addition of B_2O_3 up to 2 wt % and then a slow increase of density at 5 wt %. With 10 wt % B_2O_3 , the density increased, reaching a maximum of around 99% at 1200°C.

The above data for the YSZ samples clearly show that the densification decreases as the borate content of the additive phase increases. For example, at 1200°C, with 5 wt % CB, CB_2 and B_2O_3 , the relative densities determined were 96%, 93% and 75%, respectively. This, notwithstanding the fact that the volume % of liquid present, was in the reverse order (10.7, 10.5, 11.5 volume %, respectively). With more liquid present (10 wt % addition), however, the densities obtained were higher but followed the same pattern. This would indicate that the liquid phase becomes progressively nonwetting with respect to the YSZ phase as the borate content of the liquid is increased. This perhaps could be expected from the fact that Y_2O_3 and B_2O_3 do not form any low melting compounds, thus significantly more borate phase would be required for liquid phase densification.

On the other hand, the pure YSZ samples sintered to the 95% theoretical density at 1350°C, so that a sintering aid was less required than for the CSZ samples.

X-Ray Diffraction

X-ray diffraction analysis of specimens fired at 1200°C, showed the presence of monoclinic ZrO_2 and cubic ZrO_2 in both CSZ and YSZ when calcium metaborate, calcium tetraborate and boric anhydride (B_2O_3) were used as sintering aids. With the addition of the borates there was a decrease in the cubic phase content of the sintered products.

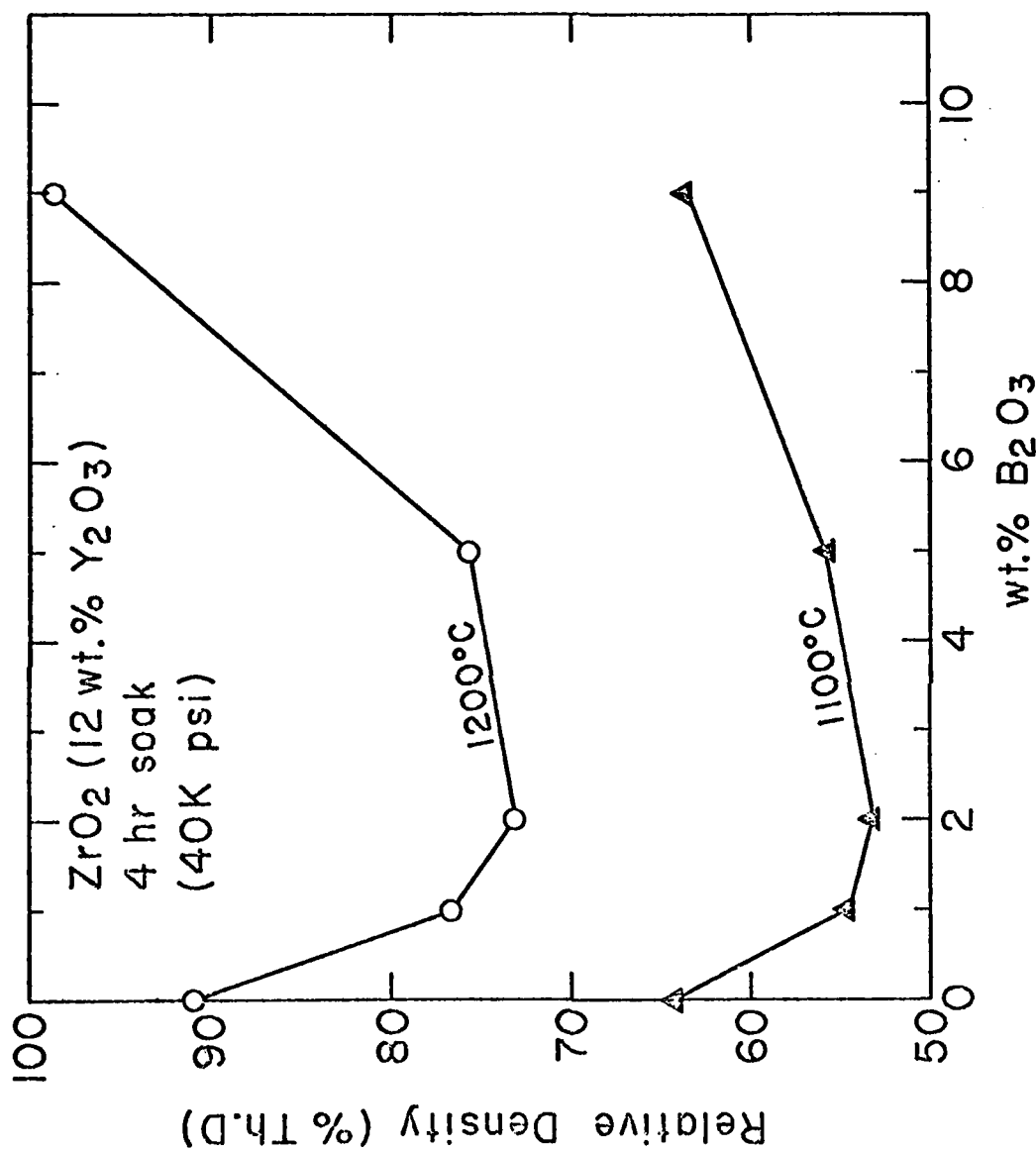


FIGURE 7. Effect of B₂O₃ addition on the densification of Y₂O₃ (12 wt.%) -stabilized ZrO₂ (YSZ) samples.

In Figure 8, the percent of monoclinic ZrO_2 phase present in sintered CSZ compacts (as estimated from the area under the major diffraction peak) is plotted against the wt % of sintering additive used. For calcium metaborate, calcium tetraborate and B_2O_3 , the amount of monoclinic ZrO_2 formed increased linearly with increased additive. The B_2O_3 addition gave considerably more monoclinic phase ($\sim 30\%$ at 5 wt %) compared to the CB addition ($\sim 10\%$ for 5 wt %) with the CB_2 values intermediate. This depletion of the cubic solid solution in CaO stabilized zirconia is due to the affinity of B_2O_3 and the borates to combine with the CaO in the ZrO_2 structure to form higher calcium borates, as discussed previously.

For the YSZ sample it can be seen from Figure 9 that the amount of destabilization of cubic ZrO_2 into the monoclinic phase at 1200 C was between 7 and 8% for 2 to 10 wt % B_2O_3 addition. With calcium metaborate the amount of monoclinic ZrO_2 at 1200 C was 7% from 2 wt% addition and rising to about 12% at 10 wt% CB addition. With calcium tetraborate addition to YSZ, the amount of monoclinic ZrO_2 formed at 1200 C was about 11, 12 and 17% from 2, 5 and 10 wt % dopant level. This data is in keeping with the observation from the density data that very little interaction takes place between the YSZ and borate phases. Some interaction between YSZ and Ca is indicated, however, and confirms the greater effectiveness of CB as a densification aid.

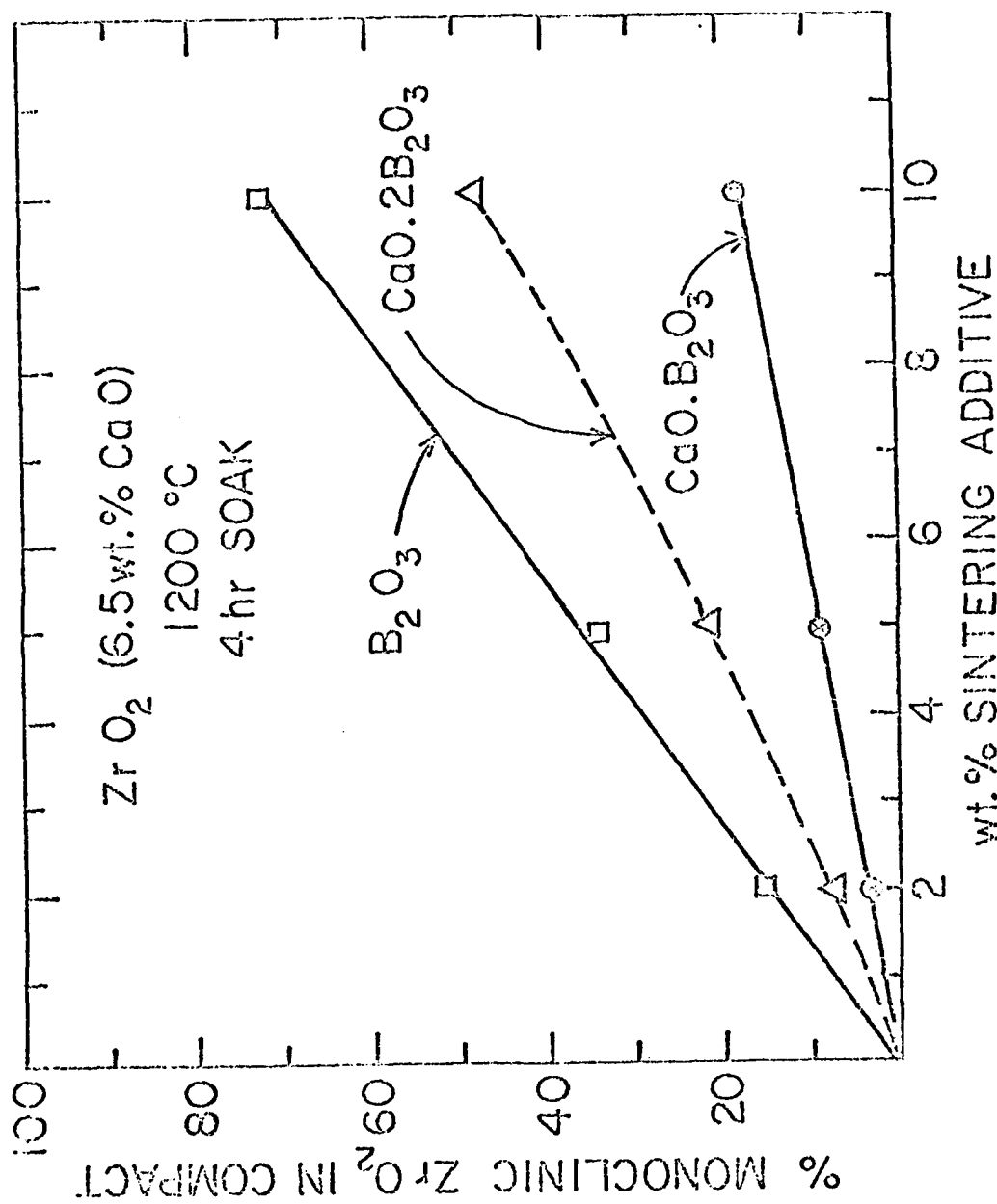
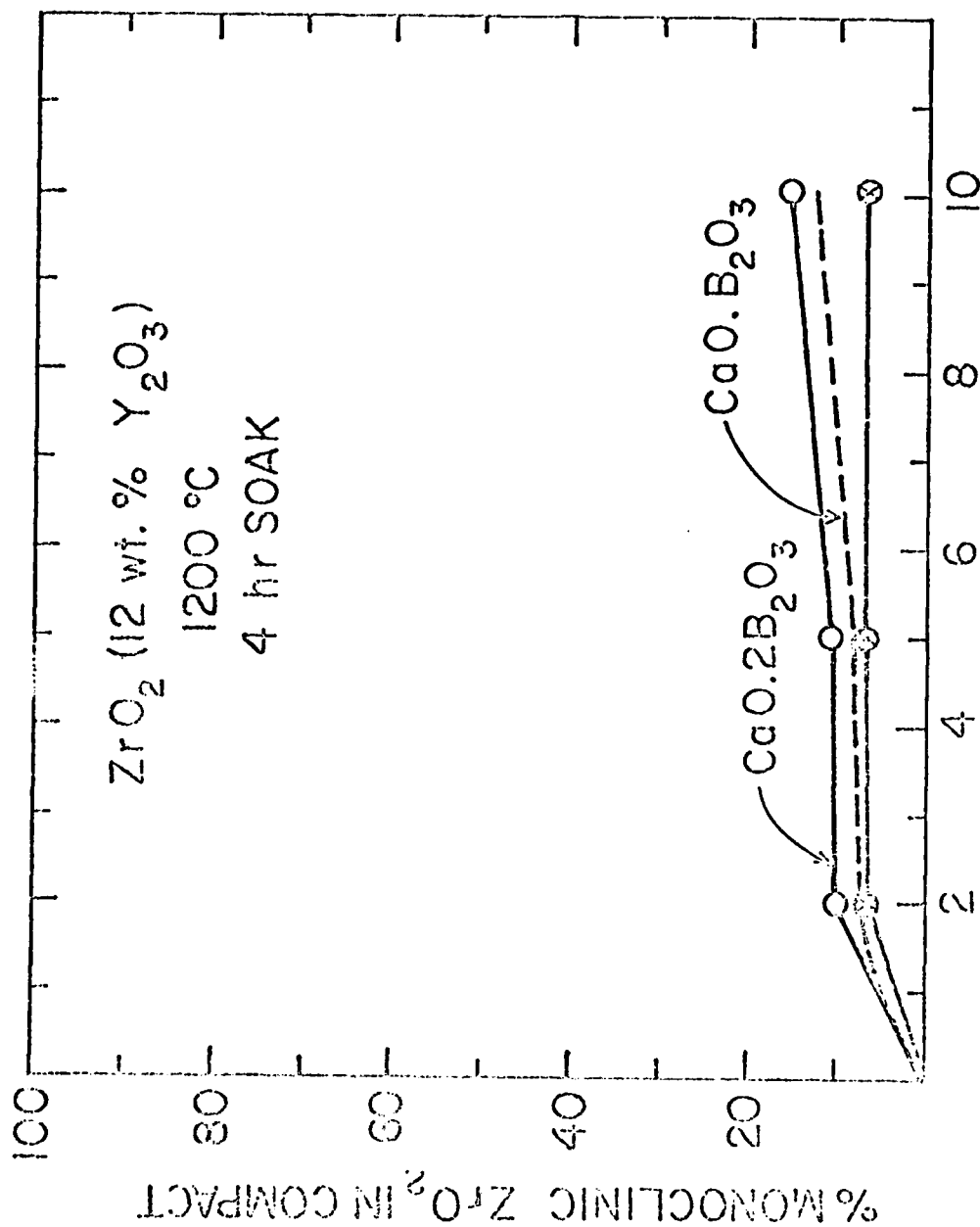


FIGURE 8. % Monoclinic ZrO_2 phase as a function of borate additives for CaO stabilized ZrO_2 samples.



WT. % SINTERING ADDITIVE

FIGURE 9. % Monoclinic ZrO_2 phase as a function of borate additives for Y_2O_3 stabilized ZrO_2 samples.

Microstructural Investigation

Figures 10a and 10b show SEM micrographs of fracture surfaces for pure CSZ and pure YSZ samples fired at 1200°C for 4 hours. All the pores appear to be located at the grain boundaries and the average grain size in the sintered samples was about .5 μm . Fractographs of the same samples fired at 1450°C for 4 hours, shown in Figure 1a and 1b, indicate that the porosities were located both at grain boundaries and within the center of grains. At 1450°C, the grain size of CSZ and YSZ samples were between 10 to 20 μm . With the pure CSZ sample, the size of the pores at the grain boundaries was about 0.5 μm and about .25 μm within the grains. However, with the pure YSZ, the pores were considerably smaller in size compared to the CSZ—about 0.25 μm at the grain boundaries and about 0.1 μm within. These micrographs for the pure stabilized zirconia fired at 1450°C were in general similar to those observed by other investigators.⁴

Figure 12a shows the SEM micrographs of fracture surface of CSZ with 5 wt % CB fired at 1200°C. As observed there are some large grains (between 5 and 10 μm) of cubic ZrO_2 , along with some very small grains (about 0.5 μm) of pure ZrO_2 , which had converted to the monoclinic form on cooling.^{26,27}

Figure 12b show the microstructure of the fracture surface of the same sample fired at 1350°C. At the higher temperature, the large grains of cubic ZrO_2 had increased in size (between 20 and 30 μm) and having small grains (between 5 and 10 μm) of pure monoclinic ZrO_2 along the grain boundaries. As shown, there was no evidence of intergranular porosity.



FIGURE 10a. SEM micrograph of fracture surface for calcia (6.5 wt%) stabilized ZrO₂-CSZ sample (sinter: 1200°C for 4 hours).



FIGURE 10b. SEM micrograph of fracture surface for yttria (12 wt%) stabilized ZrO₂-YSZ sample (sinter: 1200°C for 4 hours).

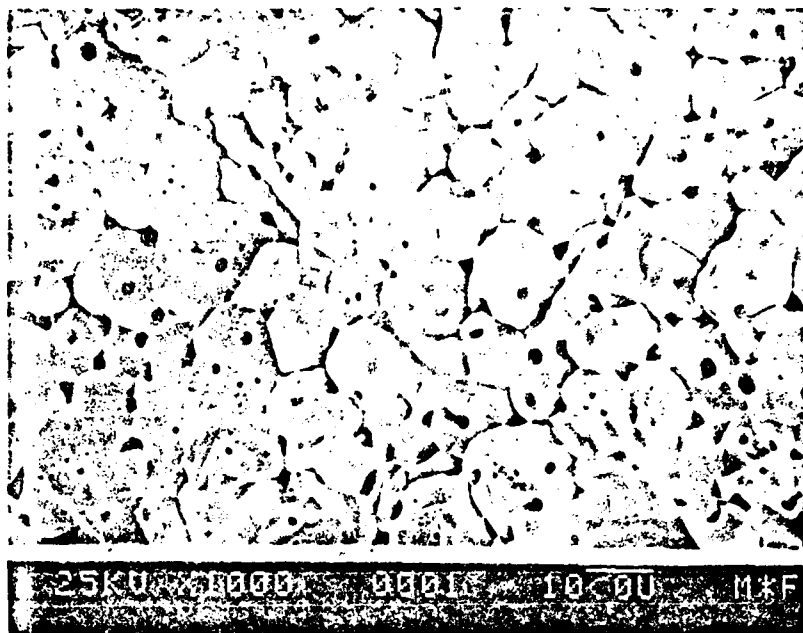


FIGURE 11a. SEM micrograph of fracture surface for calcia (6.5 wt%) stabilized ZrO₂-CSZ sample (sinter: 1450°C for 4 hours).



FIGURE 11b. SEM micrograph of fracture surface for yttria (12 wt%) stabilized ZrO₂-YSZ sample (sinter: 1450°C for 4 hours).

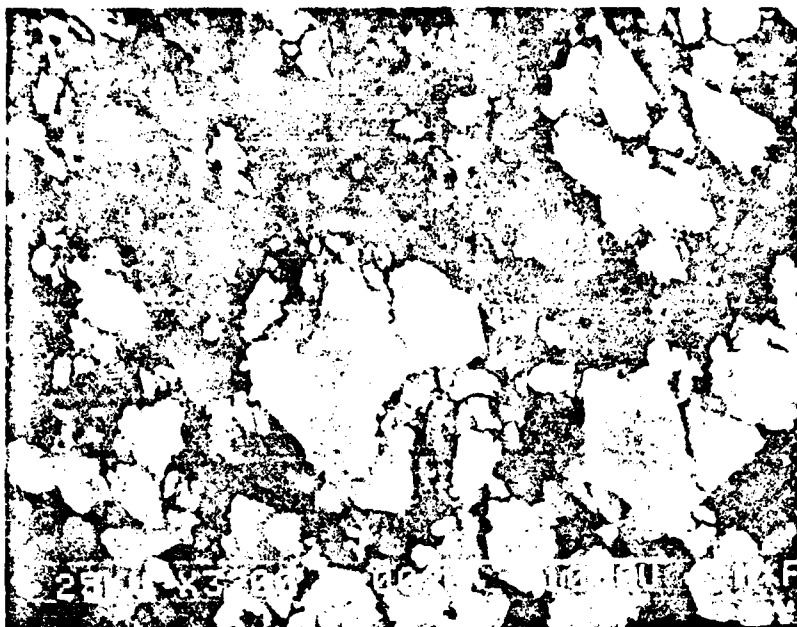


FIGURE 12a. SEM micrograph of fracture surface for CSZ + 5 wt% CB sample (sinter: 1200°C for 4 hours).

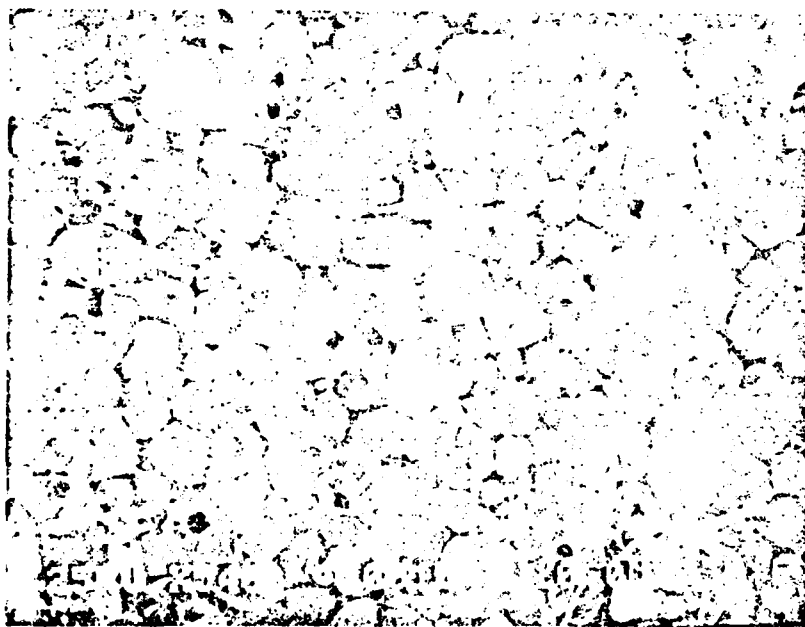


FIGURE 12b. SEM micrograph of fracture surface for CSZ + 5 wt% CR sample (sinter: 1350°C for 4 hours).

The fractograph of CSZ sample with 5 wt % CB_2 addition and sintered at 1200°C , as seen in Figure 13, indicate smaller grain growth but the presence of more monoclinic ZrO_2 than with equivalent amount of CB addition, as indicated by the much higher concentrations of small grains $\leq .5 \mu\text{m}$. This higher concentration of monoclinic ZrO_2 was also confirmed by XRD studies, as shown in Figure 8.

Fracture surfaces of CSZ samples fired at 1200°C with 10 wt % CB and CB_2 are shown in Figures 14a and 14b, respectively. As indicated by the micrographs, grain sizes with 10 wt % CB and CB_2 were considerably smaller than with 5 wt % addition level. However, the majority phase in CSZ samples with 10 wt % CB and CB_2 was pure, monoclinic ZrO_2 with small amounts of cubic ZrO_2 . Samples of CSZ with 10 wt % CB_2 addition contained more of the small grained monoclinic ZrO_2 than those with CB.

Figure 15 shows the fracture surface for the CSZ sample with 2 wt % B_2O_3 fired at 1200°C for 4 hours. The microstructure is similar to the 5 wt. % CB_2 sample, but average particle size appear to be smaller, and the amount of monoclinic phase indicated by x-ray diffraction was somewhat lower.

Figures 16a, 16b and 16c show the fracture micrographs of YSZ samples fired at 1200°C with 10 wt % B_2O_3 , CB and CB_2 , respectively. As indicated, densification obtained below 10 w/o additive was incomplete. In YSZ, B_2O_3 had the least effect on grain growth, whereas, there was indication of grain growth with 10 wt % CB and CB_2 . The latter may have a slightly greater effect on grain growth than CB.

From the microstructural observations, therefore, it appears



FIGURE 13. SEM micrograph of fracture surface for CSZ + 5 wt% CB_2 sample (sinter: 1200°C for 4 hours).



FIGURE 14a. SEM micrograph of fracture surface for CSZ + 10 wt% CB sample (sinter: 1200°C for 4 hours).

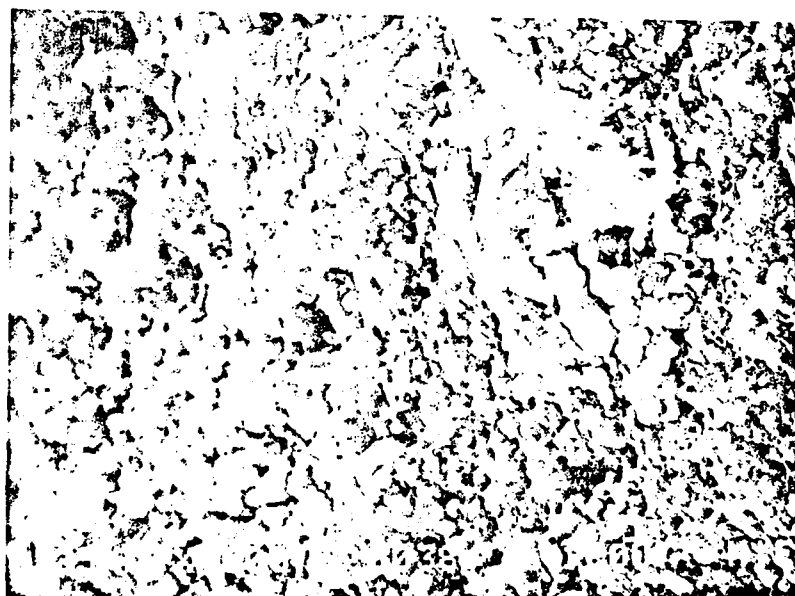


FIGURE 14b. SEM micrograph of fracture surface for CSZ + 10 wt% CB₂ sample (sinter: 1200°C for 4 hours).



FIGURE 15. SEM micrograph of fracture surface for CSZ + 2 wt% B_2C_3 sample (sinter: 1200°C for 4 hours).

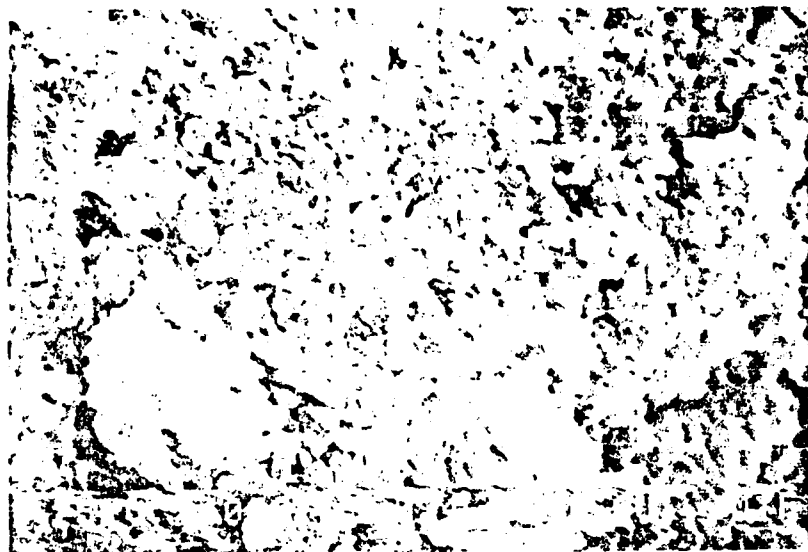


FIGURE 16a.

SEM micrograph of fracture surface for YSZ + 10 wt% B₂O₃ sample (sinter: 1200°C for 4 hrs).



FIGURE 16b.

SEM micrograph of fracture surface for YSZ + 10 wt% CB sample (sinter: 1200°C for 4 hrs).



FIGURE 16c.

SEM micrograph of fracture surface for YSZ + 10 wt% CB₂ sample (sinter: 1200°C for 4 hrs).

that for the CSZ samples there was grain growth with 5 wt % CB and CB₂, but with higher amounts of liquid at the 10 wt % level, grain growth decreased. With increasing of borates, there was gradual breakdown of the CaO-stabilized cubic ZrO₂, and at 10 wt % additive level the majority phase was the pure monoclinic ZrO₂. The YSZ samples were not much effected by the borate additions. With 10 wt % CB and CB₂ there was some grain growth and the presence of monoclinic ZrO₂ but the effects were, in general, small especially for B₂O₃ additions.

III. Summary of Results

1. Additions of 5 wt % calcium metaborate (CB) to CaO-stabilized zirconia (CSZ) gave bulk densities of 99% theoretical when sintered at 1200°C for 4 hours. There was some conversion of the cubic ZrO_2 to the pure monoclinic form at 1200°C, about 9% monoclinic being observed in the x-ray diffraction analysis.

2. With 5 wt % calcium tetraborate (CB_2) addition to CSZ, bulk densities of 100% theoretical were obtained at 1200°C for 4 hours. However, x-ray diffraction showed the conversion of about 21% of the cubic ZrO_2 to the monoclinic form.

3. Only 2 wt % B_2O_3 addition was needed to give bulk densities of 100% theoretical in CSZ samples sintered at 1200°C. The amount of monoclinic ZrO_2 present as found from x-ray analysis, was about 16%.

4. With CSZ, B_2O_3 was the most reactive additive, followed by CB_2 , the least reactive being CB.

5. Yttria-stabilized zirconia (YSZ) was far less reactive than CSZ with the calcium borates or pure B_2O_3 . Additions at 10 wt % level of CB, CB_2 and B_2O_3 were needed to obtain full densities in YSZ samples at 1200°C. Among the borates, CB_2 seemed more reactive with YSZ than CB. The least reactive was pure B_2O_3 , which showed only 8% monoclinic ZrO_2 with 10 wt % addition at 1200°C in YSZ samples, compared to 12.5 and 16% monoclinic ZrO_2 with 10 wt % CB and CB_2 , respectively. This behavior of the borates with YSZ is opposite to that of CSZ, which was most

effected by B_2O_3 , followed by CB_2 and last by CB .

6. In contrast to the results of Keler et al,¹⁶ B_2O_3 was effective as a sintering aid for CaO and Y_2O_3 stabilized ZrO_2 . This may be because of inefficient dispersion of the B_2O_3 additive in the previous investigation,¹⁶ or perhaps, due to hydration which gave porosity from the release of the water of crystallization from the B_2O_3 at higher temperatures.

7. Since partial destabilization of cubic ZrO_2 can be beneficial,^{21,22,23,24,25} pure B_2O_3 , calcium metaborate and calcium tetraborate can be used as a sintering additive for stabilized zirconia. The amount of additive used would depend on the amount of the monoclinic ZrO_2 required to produce optimum benefits in partially stabilized zirconia bodies.

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